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### Citation for published version:

Gauci, V, Blake, S, Stevenson, D & Highwood, EJ 2008, 'Halving of the northern wetland CH<sub>4</sub> source by a large Icelandic volcanic eruption', *Journal of Geophysical Research*, vol. 113.  
<https://doi.org/10.1029/2007JG000499>

### Digital Object Identifier (DOI):

[10.1029/2007JG000499](https://doi.org/10.1029/2007JG000499)

### Link:

[Link to publication record in Edinburgh Research Explorer](#)

### Document Version:

Publisher's PDF, also known as Version of record

### Published In:

Journal of Geophysical Research

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## Halving of the northern wetland CH<sub>4</sub> source by a large Icelandic volcanic eruption

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Received 31 May 2007; revised 4 March 2008; accepted 21 April 2008; published 11 September 2008.

[1] Northern temperate and high-latitude wetlands are a major source of the greenhouse gas methane (CH<sub>4</sub>). Here, we estimate the sensitivity in the strength of this source to the effects of large Icelandic volcanic eruptions such as the Laki eruption of 1783–1784. We applied spatially explicit modeled sulfate aerosol and S deposition fields from a Laki eruption simulation to a climate-sensitive model of CH<sub>4</sub> emissions from wetlands. We estimate that the combined influence on climate and S deposition from the Laki eruption halved the output of CH<sub>4</sub> from wetlands north of 30°N for the first 12 months following the eruption. The largest short-term component responsible for the CH<sub>4</sub> suppression is the aerosol-influenced surface cooling, although the effect of large-scale S deposition on CH<sub>4</sub> emissions provides a longer-term suppressive effect on emissions. Together, we estimate this combination of processes to result in an annual suppression of ~20 Tg CH<sub>4</sub> in the year of the eruption and two subsequent years. Further, the impact of the eruption on atmospheric CH<sub>4</sub> concentration extends beyond the likely duration of suppressed emission. The modeled effect of this large Icelandic eruption is consistent with ice core records of atmospheric CH<sub>4</sub> concentrations at the time and is equivalent, in size, to the current estimated suppressive effect of industrially derived S pollution on the global wetland CH<sub>4</sub> source.

**Citation:** Gauci, V., S. Blake, D. S. Stevenson, and E. J. Highwood (2008), Halving of the northern wetland CH<sub>4</sub> source by a large Icelandic volcanic eruption, *J. Geophys. Res.*, 113, G00A11, doi:10.1029/2007JG000499.

### 1. Introduction

[2] Methane (CH<sub>4</sub>) is a radiatively and chemically important atmospheric constituent, the concentration of which has varied substantially in recent times and over geologic timescales [Blunier *et al.*, 1993, 1995; Etheridge *et al.*, 1998]. Natural wetlands are the largest individual source of CH<sub>4</sub> with an estimated annual pre-industrial emission of around 160 Tg [Houweling *et al.*, 2000]. This wetland source is climate sensitive [Walter and Heimann, 2000; Gedney *et al.*, 2004; Shindell *et al.*, 2004] with temperature controlling the rates of anaerobic CH<sub>4</sub> production and aerobic CH<sub>4</sub> consumption (oxidation) [Walter and Heimann, 2000]. Further, since the water table of a wetland defines the relative proportions of CH<sub>4</sub> production (below the water table) and CH<sub>4</sub> oxidation (predominantly above the water table), wetland CH<sub>4</sub> emission is also critically dependent on precipitation.

[3] Findings from field-scale manipulation experiments have demonstrated the existence of an additional chemical control on emissions. The chronic deposition of SO<sub>4</sub><sup>2−</sup>, from acid rain, can dramatically reduce the output of CH<sub>4</sub> from

natural CH<sub>4</sub>-emitting wetlands [Dise and Verry, 2001; Granberg *et al.*, 2001; Gauci *et al.*, 2002]. Methane production and fluxes have been found to be low in a variety of anaerobic soils and sediments that share the common feature of high SO<sub>4</sub><sup>2−</sup> concentrations, for example, ocean sediments, swamps in Belize and peatlands in the Hudson Bay Lowland in North America [Albert *et al.*, 1995; Rejmankova and Post, 1996; and Reeve *et al.*, 1996]. In these systems, sulfate-reducing bacteria and methane-producing archaea occupy similar redox niches. When sulfate is not limiting, sulfate reduction forms the more energetically and, therefore, competitively superior metabolic process, thus excluding methanogenesis [Abram and Nedwell, 1978]. It is likely that the chronic deposition of SO<sub>4</sub><sup>2−</sup> on anaerobic wetland systems stimulates the formation of a competitively superior population of sulfate-reducing bacteria. This population may outcompete methane-forming microorganisms for limiting substrates, thereby reducing the production of CH<sub>4</sub> [Gauci and Chapman, 2006].

[4] Recent studies have manipulated inputs of SO<sub>4</sub><sup>2−</sup> to otherwise pristine high-latitude peatlands to assess the response of CH<sub>4</sub> emissions to acid rain levels of S deposition [Dise and Verry, 2001; Granberg *et al.*, 2001; Gauci *et al.*, 2002]. These studies, spanning natural peatlands from Sweden [Granberg *et al.*, 2001], Scotland [Gauci *et al.*, 2002] and Minnesota [Dise and Verry, 2001] yielded a consistent pattern in which increasing S deposition led to an increase in methane flux suppression at a rate which has Michaelis-Menton response characteristics [Gauci *et al.*, 2004]. Additional investigations of the effect of S deposi-

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tion on rates of sulfate reduction within peatlands across a natural S deposition gradient have shown a similar pattern. Rates of sulfate reduction increase with increasing S deposition up to deposition rates of around 15–20 kg S ha<sup>-1</sup> a<sup>-1</sup>, beyond which, sulfate reduction rates asymptote toward a constant value as sulfate reduction becomes limited by factors other than sulfate supply [Vile *et al.*, 2003]. Gauci *et al.* [2005] argued that CH<sub>4</sub> emissions from peatlands may remain suppressed for up to 5–10 years after cessation of experimental SO<sub>4</sub><sup>2-</sup> treatments owing to recycling of S within the steep redox gradients that exist within the rhizosphere of peatlands.

[5] Changes in climate and S deposition can therefore force changes in the strength of the wetland methane source and hence the atmospheric CH<sub>4</sub> load. Because certain volcanic eruptions can influence climate [e.g., Robock, 2000; Blake, 2003] and emit large amounts of S (up to tens or hundreds of Tg of SO<sub>2</sub>) that can produce widespread acid rain [Thordarson and Self, 2003], the possibility exists for perturbations in atmospheric CH<sub>4</sub> to be caused by exceptional volcanic activity.

[6] In addition, beyond influences on climate and S deposition, volcanic gas emissions during eruptions can alter levels of the hydroxyl radical (OH) [Coffey, 1996; Stevenson *et al.*, 2003], which is the dominant methane oxidant, again resulting in a change to atmospheric CH<sub>4</sub>, this time by influencing the major CH<sub>4</sub> sink rather than a source. Some of these processes have been proposed to explain the anomalous atmospheric CH<sub>4</sub> changes in 1991 and 1992 that immediately postdated the 15 June 1991 eruption of Pinatubo (Philippines). The Pinatubo eruption lofted tephra and 20 Tg of SO<sub>2</sub> into the stratosphere, creating a H<sub>2</sub>SO<sub>4</sub> aerosol veil that eventually circled the globe and increased the global mean stratospheric optical depth by up to 0.15 [Bluth *et al.*, 1997]. Dlugokencky *et al.* [1996] calculated that the resultant decrease in UV radiation led to a decrease in OH radicals, inhibiting the chemical destruction of methane and thereby allowing the unusually high CH<sub>4</sub> growth rate measured in late 1991 and early 1992. Following this, as the Pinatubo aerosol dispersed across the globe, surface cooling ensued [McCormick *et al.*, 1995] that may have reduced the wetland methane emission rate sufficiently to cause the observed rapid subsequent decrease in [CH<sub>4</sub>] [Hogan and Harriss, 1994].

[7] Unlike Pinatubo, many other eruptions inject gas only or mainly into the troposphere, where the transport and lifetime of SO<sub>2</sub> and sulfate aerosol are very different from that in the stratosphere. These eruptions can therefore induce very different phenomena. The most severe example in historical times is the Laki eruption in Iceland that erupted 15.1 km<sup>3</sup> of basaltic magma and 122 Tg SO<sub>2</sub> during the eight months from 8 June 1783 to 7 February 1784 [Thordarson *et al.*, 1996]. Most of the SO<sub>2</sub> (91 Tg) was emitted in the first two months of the eruption [Thordarson and Self, 2003]. As a result of the eruption, the summer of 1783 was unpleasant over northern latitudes [Thordarson and Self, 2003] with the effects including acid damage to crops and other plants [Grattan and Pyatt, 1994], the poisoning of livestock, poor air quality, and increased human mortality rates in Iceland and Europe [Grattan *et al.*, 2003; Witham and Oppenheimer, 2004]. Given that the Laki eruption maintained a prolonged and substantial sup-

ply of SO<sub>2</sub> across northern latitudes, the possibility arises that this may have suppressed methane emissions from wetlands for a number of years [Gauci *et al.*, 2005]. Iceland lies close to the latitudes of the northern wetland methane source and has produced at least 9 eruptions that injected more than 20 Tg SO<sub>2</sub> into the atmosphere in the last 10,000 years [Thordarson *et al.*, 2003]. Here we seek to quantify the response of the wetland CH<sub>4</sub> source to climatic and S deposition perturbations brought about by large Icelandic volcanic eruptions of this type. We use the most recent of these, the Laki eruption of 1783–1784, as our model event.

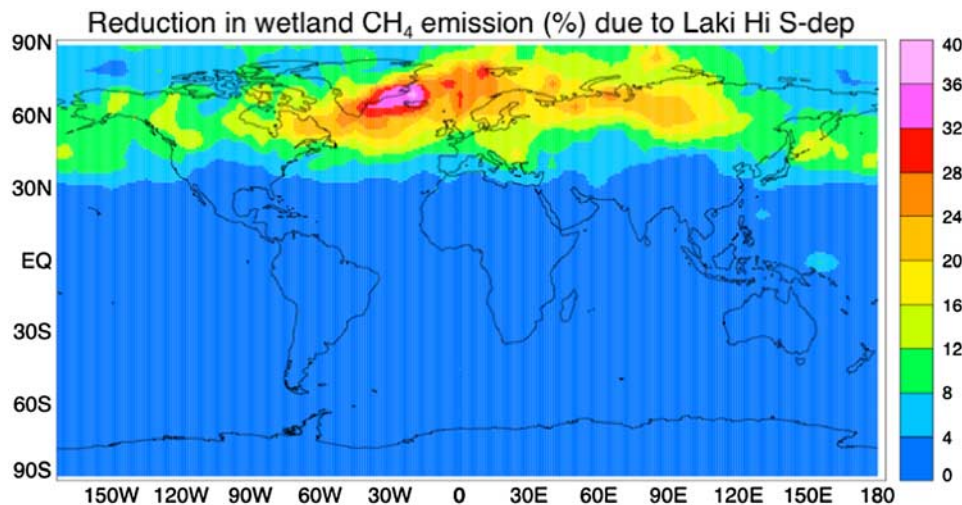
## 2. Methods

[8] We estimated the impact of a large Icelandic eruption on the wetland CH<sub>4</sub> source using a combination of: (1) a 3-D chemistry-transport model simulation of the fate of the SO<sub>2</sub> emitted during the Laki eruption [Stevenson *et al.*, 2003]; (2) a climate model simulation of the eruption period and immediate aftermath, using sulfate aerosol fields generated by the chemistry model [Highwood and Stevenson, 2003]; (3) a simplified spatially explicit regression model of CH<sub>4</sub> emission from natural wetlands [Dlugokencky *et al.*, 2001]; and (4) a model of the % suppression of CH<sub>4</sub> emission from sulfate manipulated wetlands spanning a range of S deposition [Gauci *et al.*, 2004]. The following sections describe this approach in greater detail.

### 2.1. Modeled Laki S Deposition and Climate Impact

[9] The Laki SO<sub>2</sub> plume and associated atmospheric chemistry was simulated by a chemistry-transport model within a University of Edinburgh version of the UK Met Office STOCHEM CTM, STOCHEM-Ed as described in detail by Stevenson *et al.* [2003]. We used the ‘Laki–“Hi/Long”’ emission plume scenario which had the longest aerosol perturbation decay time (10 months) and largest climate impact of the scenarios employed by Highwood and Stevenson [2003]. The model has a high-resolution tropopause region and a detailed sulfur chemistry scheme. The simulated SO<sub>2</sub> plume spread over much of the Northern Hemisphere poleward of ~40°N. Total S deposition was calculated as the sum of wet and dry deposition of SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>; the latter was generally insignificant. About 70% of deposited sulfur was deposited as SO<sub>2</sub>. Detailed SO<sub>4</sub><sup>2-</sup> aerosol and SO<sub>4</sub><sup>2-</sup> deposition distributions are described by Stevenson *et al.* [2003] and are consistent with measurements of SO<sub>4</sub><sup>2-</sup> in Greenland ice [Stevenson *et al.*, 2003]. Radiative forcing and climate response to these aerosol distributions were calculated using the Reading Intermediate General Circulation Model (IGCM) which is described in detail by Highwood and Stevenson [2003]. Peak Northern Hemisphere mean direct radiative forcing was estimated as –5.5 W m<sup>-2</sup> in August 1783, normally a peak time of year for Northern Hemispheric wetland CH<sub>4</sub> emission. The model also estimated that, over the 12 months spanning most of the eruption, the Northern Hemisphere experienced a mean temperature anomaly of –0.21 K which is in broad agreement with temperature observations made during 1783 [Highwood and Stevenson, 2003]. Other Laki eruption models simulate a much larger stratospheric input of SO<sub>4</sub><sup>2-</sup> [Chenet *et al.*, 2005; Oman *et al.*, 2006a]





**Figure 1.** Percentage suppression ‘mask’ for wetland CH<sub>4</sub> emission for the period 1 May 1783 to 30 April 1784 during and following the 1783–1784 Laki eruption based on sulfur deposition scenario ‘Laki Hi’ [Stevenson *et al.*, 2003].

with larger radiative forcing so we consider our approach to be a conservative assessment of the role of Icelandic eruptions in regulating wetland CH<sub>4</sub> emissions.

## 2.2. Effect of Modeled Climate Perturbation on Wetland CH<sub>4</sub> Emission

[10] We applied a regression simplification of a process-based climate sensitive model of CH<sub>4</sub> emission from wetlands [Dlugokencky *et al.*, 2001; Gauci *et al.*, 2004]. The regression model captures the majority of the variability in CH<sub>4</sub> emissions induced by changes in temperature and precipitation ( $r^2 = 0.8$ ) and successfully reproduced observed atmospheric CH<sub>4</sub> concentration anomalies in the 1990s [Dlugokencky *et al.*, 2001]. CH<sub>4</sub> emissions were calculated using this regression model and with input of monthly temperature and precipitation anomalies generated by the Laki climate simulation for the year of the Laki eruption (May 1783 to April 1784) and for the following two years, which also experienced slightly negative radiative forcings [Highwood and Stevenson, 2003]. Total annual pre-Laki CH<sub>4</sub> emissions were scaled so as to equal the estimated pre-industrial levels and post-Laki emissions were treated with the same scaling factor [Gauci *et al.*, 2004].

## 2.3. Effect of S Deposition on Wetland CH<sub>4</sub> Emission

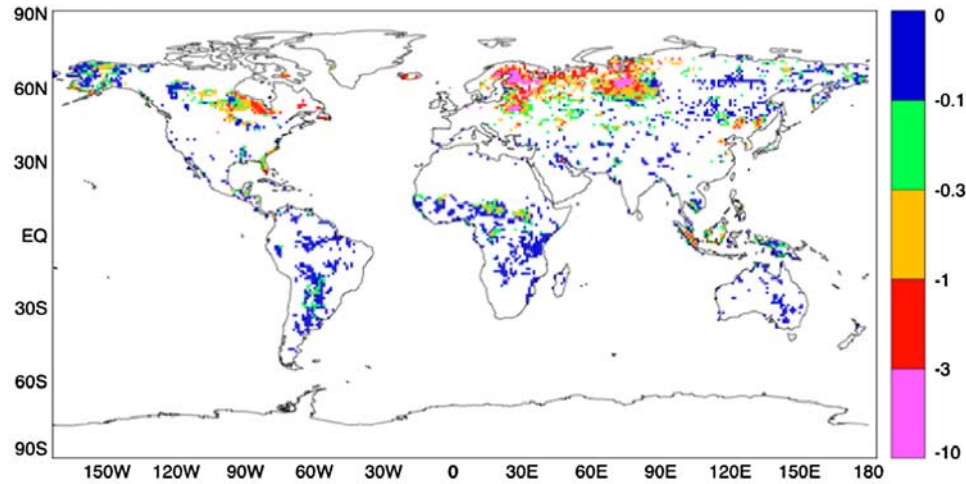
[11] We applied a Michaelis-Menton model of the effect of sulfate deposition on CH<sub>4</sub> emission which Gauci *et al.* [2004] derived from independent ‘acid rain’ simulation experiments in the United States, the United Kingdom and Sweden. This synthesis yielded a pattern of CH<sub>4</sub> emission response to S deposition where suppression rapidly increased with increasing S deposition up to a sulfate deposition rate of 15–20 kg S ha<sup>-1</sup> a<sup>-1</sup> after which suppression increased but at a shallower rate of change to a maximum suppression of ~40% [Gauci *et al.*, 2004]. We applied this Michaelis-Menton model to assess the impact of annualized modeled Laki deposition on Laki climate-impacted wetland CH<sub>4</sub> emission. This demonstrates that many wetland rich regions of the Northern Hemisphere may have experienced a reduction in CH<sub>4</sub> emission of between 8 and 24%

(Figure 1). The spatially explicit model output of wetland CH<sub>4</sub> emission and S deposited from the tropospheric Laki simulation were combined using the Michaelis-Menton model so that the effect of Laki-derived S on the wetland CH<sub>4</sub> source could be calculated for the eruption year of 1783–1784. It was assumed that all dry deposited S (i.e., SO<sub>2</sub> the dominant deposition fraction) is converted to sulfate upon deposition on wetland [Gauci *et al.*, 2004]. Given that S deposition is known to suppress CH<sub>4</sub> emissions for a minimum of 2 years after a deposition event [Gauci *et al.*, 2005] we applied an equal suppressive effect of S to the two years after the eruption year (i.e., 3 years of suppression in total).

## 3. Results and Discussion

[12] The total combined effect of Laki aerosol climate impact and deposition of S on wetlands was sufficient to suppress annual CH<sub>4</sub> emission from an estimated pre-industrial source of 160 Tg a<sup>-1</sup> [Houweling *et al.*, 2000] to 137 Tg a<sup>-1</sup> for the Laki eruption year between May 1783 and April 1784. This 23 Tg CH<sub>4</sub> suppression (a 14% reduction in emissions) is a comparable proportion to the estimated effect of current industrially derived sulfur pollution on the wetland CH<sub>4</sub> source [Gauci *et al.*, 2004]. When considering the effect of S deposition alone, wetlands in Scandinavia, central Europe and the West Siberian Lowland were most impacted, experiencing a reduced output of CH<sub>4</sub> of up to 10 g CH<sub>4</sub>/m<sup>2</sup>/a (Figure 2). Other regions to also experience significant reduction in CH<sub>4</sub> emissions due to Laki S deposition include the Hudson Bay Lowland and other parts of northeast Canada (Figure 2). Overall, the Laki-derived cooling was the largest contributory factor in reducing emissions, ~14 Tg, as opposed to an 8.8 Tg suppression contributed via the Laki S deposition effect on the competitive exclusion of methanogenesis (Figure 3). The majority of the total suppression occurred in latitudes north of 30°N, where wetland CH<sub>4</sub> emissions were halved from ~42 Tg to ~22 Tg, of which 80% was the result of aerosol induced cooling during the eruption year (Figure 4).

### Change in Wetland CH<sub>4</sub> emission due to Laki Hi S dep (g CH<sub>4</sub>/m<sup>2</sup>/yr)



**Figure 2.** Change in wetland CH<sub>4</sub> emission due to ‘Laki Hi’ S-dep (g CH<sub>4</sub> m<sup>-2</sup> a<sup>-1</sup>) for the period 1 May 1783 to 30 April 1784 during and following the 1783–1784 Laki eruption.

Although the northern latitude (>30°N) aerosol impact on the CH<sub>4</sub> source diminished 2 years after the end of the eruption (Figure 4), a small cooling component in the tropics had a notable effect on tropical CH<sub>4</sub> emissions and therefore on global CH<sub>4</sub> emission from wetlands (as the tropical CH<sub>4</sub> source is so large) (Figure 3).

[13] Our model predicts a global drop in CH<sub>4</sub> emission rate of ~20 Tg a<sup>-1</sup> for 3 years. The effect of S deposition may have lingered beyond that time, owing to recycling of S [Gauci *et al.*, 2005], such that CH<sub>4</sub> emission rates continued to be lower than normal by ~10 Tg a<sup>-1</sup>.

[14] What effect might the reduced source strength have had on the global atmospheric CH<sub>4</sub> load, and can such an effect be seen in the ice core record of 18th century methane? Given the irregular sampling and time-averaged nature of the ice core record [Etheridge *et al.*, 1998], this discussion is limited to exploring a simple mathematical model of the response of atmospheric methane to a period of lowered source strength. The model makes the simplifying assumption that the degree of suppression remains constant for a finite time and then instantaneously recovers.

[15] The effect of a change in emission rate on the atmospheric load is modeled using the equation describing the methane budget [Etheridge *et al.*, 1998]:

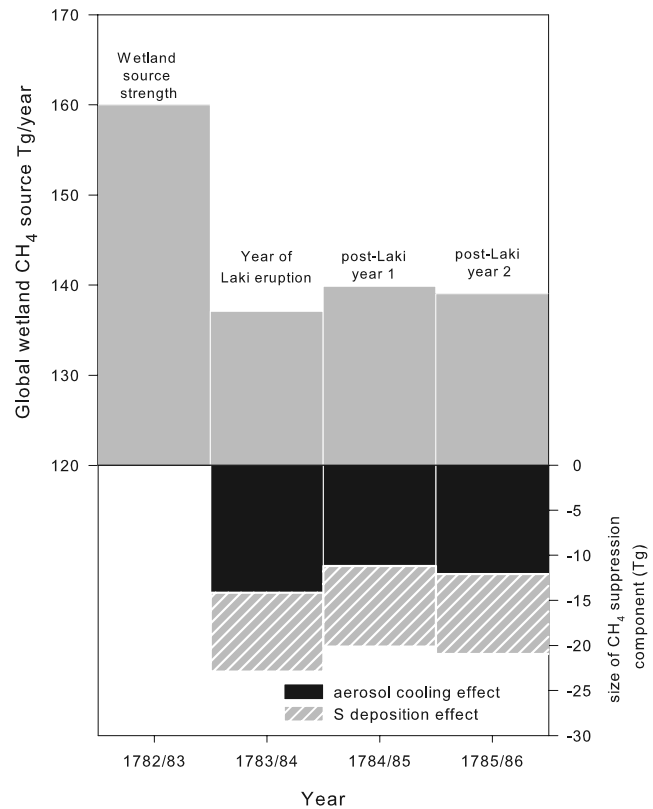
$$\frac{dB}{dt} = S - \frac{B}{T}, \quad (1)$$

where  $B$  is the methane burden in the atmosphere (Tg),  $t$  is time (year),  $S$  is the methane source emission rate (Tg a<sup>-1</sup>), and  $T$  is the lifetime of methane in the atmosphere (year). The mixing ratio [CH<sub>4</sub>] in ppbv is related to the burden,  $B$ , by [CH<sub>4</sub>] =  $B/c$  where the constant  $c = 2.767$  Tg ppbv<sup>-1</sup> [Fung *et al.*, 1991].

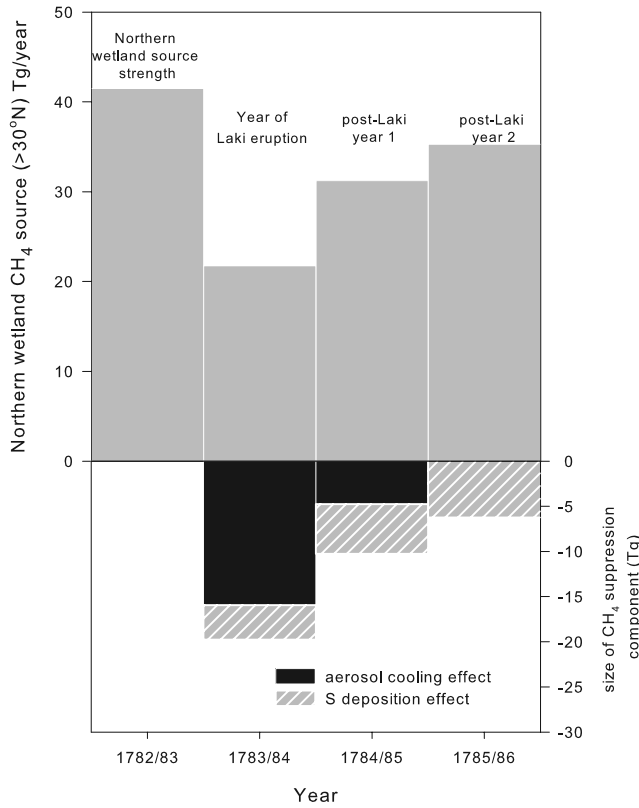
[16] From ice core records, it is known that [CH<sub>4</sub>] was fairly constant until ~1730 and thereafter increased gradually [Etheridge *et al.*, 1998] as wetlands warmed as the world exited the Little Ice Age and then, later that century, as emission rate became augmented by anthropogenic sources of steadily increasing strength. Our model therefore

assumes up until  $t = 0$  (equivalent to the time when anthropogenic sources started to be significant),  $S$  is constant ( $S_0$ ) and the methane burden is at steady state. After  $t = 0$  and until  $t_d$ , the source emission rate increases linearly with time at a constant rate  $a$ :

$$S = S_0 + at. \quad (2)$$



**Figure 3.** Effect of Laki derived aerosol and S deposition effects on the total global wetland CH<sub>4</sub> source for the years 1783–1786.



**Figure 4.** Effect of Laki derived aerosol and S deposition effects on the northern wetland CH<sub>4</sub> source (>30°N) for the years 1783–1786.

At  $t_d$  the background emission rate drops from  $S_0$  to  $S_s$  owing to the suppressive effects modeled in section 2 but the imposed anthropogenic rate ( $a$   $t$ ) stays the same. This situation continues until  $t_r$  when the background supply recovers and returns to  $S_0$ . So, for  $t_d < t \leq t_r$ ,

$$S = S_s + at \quad (3)$$

and for  $t_r < t$ ,

$$S = S_0 + at. \quad (4)$$

Solving (1) and (2) for the initial condition

$$B = B_0 = TS_0 \text{ at } t = 0$$

gives, in the time interval  $0 \leq t \leq t_d$ ,

$$B = TS_0 + aTt - aT^2(1 - \exp(-t/T)) \quad (5a)$$

and for  $t_d \leq t \leq t_r$

$$B = TS_s + a(tT - T^2) + [T(S_0 - S_s) + aT^2 \exp(-t_d/T)] \cdot \exp(-(t - t_d)/T) \quad (5b)$$

and for  $t_r \leq t$

$$B = TS_0 + atT - aT^2(1 - \exp(-t/T)) + T(S_0 - S_s) \cdot [\exp(-(t - t_d)/T) - \exp(-(t - t_r)/T)]. \quad (5c)$$

The following example, using figures appropriate to Laki, illustrates the behavior of the model.

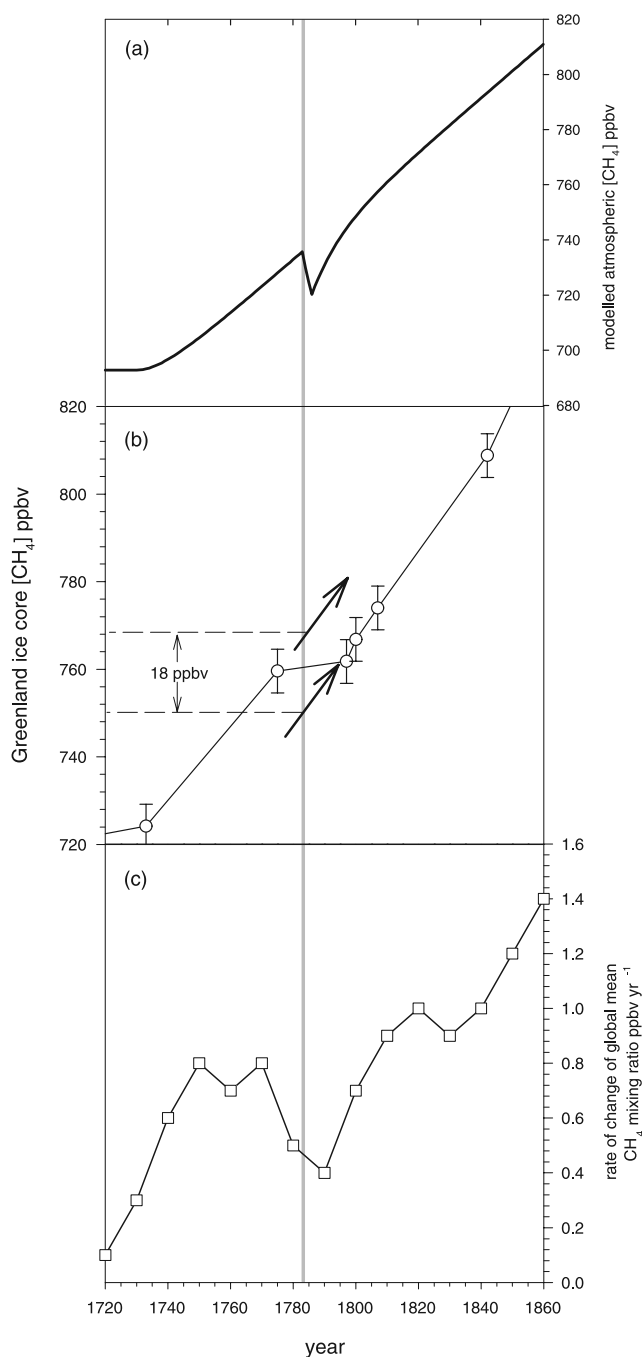
[17] From *Etheridge et al.* [1998], the residence time  $T = 9$  years and the average  $[\text{CH}_4] = 693$  ppbv for 1010 to 1730 AD. This is equivalent to  $B = 1918$  Tg and, from (1),  $S_0 = 213$  Tg  $\text{a}^{-1}$ . The overall increase in  $[\text{CH}_4]$  after 1730 ( $t = 0$ ) can be explained by setting  $a = 0.3$  Tg  $\text{a}^{-2}$ . Using the calculated decrease in methane emission rate of  $\sim 20$  Tg  $\text{a}^{-1}$  for 3 years (Figure 3) gives  $S_s = 193$  Tg  $\text{a}^{-1}$ . The start and end of methane suppression are set at  $t_d = 53$  years (1783 AD) and  $t_r = 56$  years (1786 AD). We considered the possible effects of the Laki eruption on the atmospheric CH<sub>4</sub> sink to evaluate whether the CH<sub>4</sub> residence time ( $T$ ) required alteration. Zonal mean OH is estimated to have been depleted by up to 18% at high latitudes in the middle to upper troposphere during June, July and August of 1783 (i.e., the first quarter of the eruption year) as a result of gas-phase conversion of SO<sub>2</sub> to aerosol through OH oxidation [Stevenson et al., 2003]. This will have slightly decreased CH<sub>4</sub> oxidation, and lengthened the CH<sub>4</sub> lifetime, providing a small positive influence on the atmospheric CH<sub>4</sub> growth rate. However, as methane oxidation is strongly temperature dependent (it proceeds faster at higher temperatures), most methane is oxidized in the tropical lower atmosphere, a region relatively unperturbed by the Laki eruption, so the impact on CH<sub>4</sub> lifetime was probably insignificant.

[18] The model yields an exponential decline in  $[\text{CH}_4]$  after the start of the period of reduced methane emission, followed by an exponential recovery once the suppressive effect of sulfate deposition is removed (Figure 5a). The maximum amplitude of the lowered  $[\text{CH}_4]$  is about 18 ppbv and it takes about 20 years for the concentrations to return to the levels expected had there not been a 3-year-long episode of suppressed emission. The modeled perturbation of atmospheric methane concentration is of a size and duration that would make it readily detectable by routine present-day methane monitoring programs [e.g., Dlugokencky et al., 2003]. However, the only information on 18th century atmospheric methane comes from air trapped in Greenland and Antarctic ice, with samples being averages over a few years at an irregular frequency. Figure 5b shows that a hiatus in atmospheric methane, marked by a stalling of the overall trend of increasing methane, is coincident with the Laki eruption. While other factors may have affected CH<sub>4</sub> emissions to the atmosphere around the time of Laki, for example, failure of the African and Indian monsoon [Oman et al., 2006b], (i.e., areas represented in our wetland distribution data set with few CH<sub>4</sub> emitting wetlands) other, similar drying events in recent times such as the 1997/1998 El Niño have tended to boost terrestrial CH<sub>4</sub> emissions through increases in biomass burning [van der Werf et al., 2004]. The size and duration of the drop in  $[\text{CH}_4]$  predicted by our model is consistent with the sparse available measurements in the ice core record.

#### 4. Summary and Implications

[19] The Laki eruption coincided with a halting in the rate of increase in Northern Hemisphere (NH) CH<sub>4</sub> concentration as recorded in Greenland ice (Figure 5b) [Etheridge et al., 1998]. The global mean CH<sub>4</sub> mixing ratio as calculated





**Figure 5.** (a) Modeled variation in atmospheric methane concentration before, during and after an episode of reduced emission during a period of otherwise constantly increasing emission rate. See text for further explanation. (b) Ice core records of 18th and 19th century atmospheric CH<sub>4</sub> concentration recorded in Greenland ice cores (with errors of  $\pm 5$  ppbv), arrows indicate long-term trend in [CH<sub>4</sub>] growth rate before and after the Laki eruption. (c) Annual rate of change in global mean CH<sub>4</sub> methane mixing ratios (derived from smoothed, globally adjusted and interpolated spline fit of Antarctic ice core data) (Data for Figures 5b and 5c are derived from Etheridge *et al.* [1998]). Vertical gray line indicates the eruption year.

from the Antarctic record also demonstrates a reduction in growth rate (Figure 5c) [Etheridge *et al.*, 1998]. We estimate that the reduction in recorded NH atmospheric [CH<sub>4</sub>] growth rate, during a time period when there was a general pattern of increasing [CH<sub>4</sub>] due to a growth in human influence over the methane cycle and a warming as the world exited the Little Ice Age, amounts to a relative downward shift in the pre- and post-Laki [CH<sub>4</sub>] growth trajectory of  $\sim 18$  ppbv (Figure 5b). This shift in atmospheric [CH<sub>4</sub>] growth corresponds to a decrease in the global methane burden of  $\sim 60$  Tg (based on the conversion factor from Fung *et al.* [1991]) during the period of the Laki eruption. While there are many factors which may impact on atmospheric [CH<sub>4</sub>], this reduction in the atmospheric CH<sub>4</sub> burden is consistent with our modeled estimates of long-term wetland CH<sub>4</sub> emission response to the Laki eruption (Figure 3).

[20] The Laki eruption was the largest eruption in terms of the mass of SO<sub>2</sub> emitted to the atmosphere over the last few centuries. Larger eruptions in geologically recent time are the Eldgja (AD 934–950) and Thjorsa ( $\sim 8.6$  ka) eruptions in Iceland that released about 220 and 150 Tg SO<sub>2</sub> respectively [Thordarson and Self, 2003]. In ancient times sulfur emission associated with even larger flood basalt eruptions will have far exceeded those experienced during these Icelandic eruptions. The Siberian Trap eruptions associated with the largest extinction event in Earth's history at the end of the Permian Period ( $\sim 250$  Ma before present) may have exceeded estimates of emissions from individual flood basalt eruptions such as the Roza eruption (part of the Columbia River Basalts, USA) ( $\sim 14.7$  Ma) as well as Deccan eruptions (India,  $\sim 65$  Ma). Estimates of annual sulfur emission from these events range from  $\sim 600$  Tg S a<sup>-1</sup> for the Roza eruption [Thordarson and Self, 1996] to a maximum  $\sim 1700$  Tg S a<sup>-1</sup> for a Deccan eruption [Self *et al.*, 2006] and probably lasted for a decade or more. Assuming equal hemispherical distribution of deposited sulfur, deposition rates, in the form of both dry SO<sub>2</sub> deposition and wet 'acid rain' approximate to 24 and 67 kg S ha<sup>-1</sup> a<sup>-1</sup> for the two eruption examples respectively. These rates exceed the point beyond which SO<sub>4</sub><sup>2-</sup> supply eliminates S limitation on sulfate reduction [Vile *et al.*, 2003] and so suppression of CH<sub>4</sub> emission will have achieved its maximum value of  $\sim 40\%$  or, in Michaelis-Menton terminology, a  $V_{\max}$  of 38.6% suppression [Gauci *et al.*, 2004]. This mechanism, in addition to the effect of aerosol cooling on the wetland CH<sub>4</sub> source, will have been particularly significant during pre-industrial times when methane emissions to the atmosphere were dominated by fluxes from natural wetlands and in particular during the early Eocene [e.g., Beerling and Valdes, 2002, 2003; Pancost *et al.*, 2007]. Given that simulated acid rain rates of S deposition and large experimental inputs of sulfate to rice paddies (an analog of tropical wetland ecosystems) have succeeded in suppressing as much as 70% of CH<sub>4</sub> emissions [Denier van der Gon *et al.*, 2001; Gauci *et al.*, 2008] we suggest that such events would have caused the terrestrial contribution of CH<sub>4</sub> to the atmosphere to halve for at least the duration of the eruption.

[21] **Acknowledgments.** V.G. would like to thank Mike Rampino for early discussions which led to this work, Bernadette Walter for provision of

the CH<sub>4</sub> emission model, and Domenic Ferretti for thoughtful advice. We would like to acknowledge the input of Elaine Matthews in the development of the CH<sub>4</sub> emission model. The work was funded by an Open University Research and Development Grant to V.G. and S.B. D.S. acknowledges support from Natural Environment Research Council (NERC) and the Environment Agency for fellowship support (NER/J/S/2000/00840, P4-F02). The authors would also like to acknowledge the input of two anonymous reviewers and the thorough comments of the Associate Editor.

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